

Superconductivity and Dirac Fermions in 112-phase Pnictides

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This article reviews the status of current research on the 112-phase of pnictides. The 112-phase has gained augmented attention due to the recent discovery of high-temperature superconductivity in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ with a maximum critical temperature $T_c \sim 47\text{ K}$ upon Sb substitution. The structural, magnetic, and electronic properties of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ bear some similarities with other superconducting pnictide phases, however, the different valence states of the pnictogen and the presence of a metallic spacer layer are unique features of the 112-system. Low-temperature superconductivity which coexists with antiferromagnetic order was observed in transition metal (Ni, Pd) deficient 112-compounds like CeNi_xBi_2 , LaPd_xBi_2 , LaPd_xSb_2 , LaNi_xSb_2 . Besides superconductivity, the presence of naturally occurring anisotropic Dirac Fermionic states were observed in the layered 112-compounds SrMnBi_2 , CaMnBi_2 , LaAgBi_2 which are of significant interest for future nanoelectronics as an alternative to graphene. In these compounds, the linear energy dispersion resulted in a high magnetoresistance that stayed unsaturated even at the highest applied magnetic fields. Here, we describe various 112-type materials systems combining experimental results and theoretical predictions to stimulate further research on this less well-known member of the pnictide family.

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The discovery of superconductivity in the pnictide family of superconductors LaOFeP [1] has fuelled research on the Fe-based superconducting compounds after the observation of a critical temperature of $T_c \sim 26\text{ K}$ in the isostructural compound $\text{La}(\text{O}_{1-x}\text{F}_x)\text{FeAs}$ [2], which was soon increased up to 43 K [3] under the application of high pressure [4]. Very soon, an even higher T_c of 54 K was observed in $\text{SmFeAsO}_{1-x}\text{F}_x$ [5, 6]. With different levels of doping and elemental substitutions T_c values of $55\text{--}58\text{ K}$ [7–10] were observed in several other compounds in the 1111-family of pnictides. In the next few years, superconductivity was found in various other Fe-based pnictide systems like $(\text{Ba},\text{K})\text{Fe}_2\text{As}_2$ (122-type) [11], FeSe (11-type) [12], LiFeAs (111-type) [13–15] and, most recently, $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ (112-type) with a T_c of 38 K [16–18]. The fundamental interest in these materials lies in understanding the mechanism behind the coexistence of superconductivity and magnetism. The high critical fields and isotropic critical currents [19–21] could be of interest for electrical power and magnetic applications. Apart from the presence of Fe in these compounds, which is believed to be harmful for conventional superconductivity, the uniqueness lies in the origin of superconductivity due to the presence of the Fe-3d electrons [4].

Although there are several structurally different phases of pnictides, they all contain a common Fe-pnictogen (Pn) layer in a tetrahedral arrangement that is separated by blocking layers. The composition of the blocking layer is believed to affect the superconducting properties [22]. The Fe- Pn (or Fe- Ch) layers are tetrahedrally coordi-

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nated by the Pn or Ch (chalcogenide) atoms, and highest critical temperatures were observed for an ideal tetrahedral arrangement [23] with the Fe-As-Fe bond angle closest to 109.47° . Similar to the high- T_c Cuprates, the pnictides are also quasi-two-dimensional with reduced electronic coupling along the c -axis, and the appearance of superconductivity is observed upon the suppression of the antiferromagnetic order [24]. In comparison to Cuprates, however, the range of superconducting materials is much larger in case of the pnictides offering a huge range of chemical substitution possibilities [25]. Due to the limited availability of high-quality and larger sized single crystals [22], research was focussed on the 1111- and 122-type compounds. Recently, significant interest has shifted to 11-type FeSe thin films [26], where evidence of strain induced interfacial superconductivity was observed up to a maximum $T_c \sim 109$ K [27].

A prediction of the existence of a 112-type pnictide phase was made by Shim *et al.* [28] in the hypothetical compounds $BaFeAs_2$ and $BaFeSb_2$ with metallic blocking layers unlike other pnictide systems where these layers are insulating. While these compounds remain elusive, the related compound $SrMnBi_2$ was synthesized [29–31] as single crystals with physical and structural similarities to $BaFeAs_2$. Despite having a large Néel temperature ($T_N \sim 290$ K), no evidence of superconductivity was observed in $SrMnBi_2$. Band structure calculations suggested the presence of anisotropic Dirac fermions in the Bi square net layer which was experimentally confirmed later through the observation of quantum oscillations and angle-resolved photoelectron spectroscopy (ARPES) measurements [31].

Superconductivity in the 112-type pnictide was first reported in the $CeTMPn_2$ (TM = transition metal, Pn = pnictogen) family of intermetallic compounds with $T_N \sim 5$ K although several heavy-fermion superconductors with layered tetragonal structures were known earlier [32]. Superconductivity in $CeNi_xBi_2$ with $T_c \sim 4.2$ K [33, 34] was claimed to originate from Ni deficiency, as no evidence of bulk superconductivity was observed in the parent compound $CeNiBi_2$ [35–37]. However, it has been suggested from the coexistence of light and heavy carriers that the superconducting charge carriers are hosted by the pnictogen square net layer [33]. The presence of superconductivity with low superconducting volume fraction (SVF) were also observed in $LaNi_xBi_2$ (SVF = 1–3%) [38, 39], $NdNi_xBi_2$ (SVF = 14%) [33], and YNi_xBi_2 [33] (SVF = 17%) [33].

Interest in the 112-system has grown considerably after the discovery of a high T_c of 34 K in $Ca_{1-x}La_xFeAs_2$ [16] and in $Ca_{1-x}Pr_xFeAs_2$ with $T_c \sim 20$ K [40]. Subsequently, it was reported that adding a small amount of P (0.5%) and Sb (1%) substituting As in the parent compound leads to a drastic enhancement of T_c in $Ca_{1-x}La_xFeAs_2$ to 41 K and 43 K, respectively [17]. Later, it was revealed that a larger level of Sb doping can further enhance T_c to 47 K in $Ca_{1-x}La_xFe(As_{1-y}Sb_y)$ [18] which is higher than the maximum T_c observed in

bulk 122, 11, 111-type pnictides so far. One interesting fact about the superconductivity in the 112-phase is the existence of mixed-valance states of the pnictogen [33, 38] which has different valencies in the Pn square net layer and the metal-pnictogen layers.

In the past two years, research interest again increased for $Ca_{1-x}La_xFeAs_2$ [41–54] due to the availability of single crystals, high- T_c in the bulk phase, and the possibility of a range of substitutions. Significant amount of research work was done earlier in other 112-type materials like $LaPd_xSb_2$ [55], $LaPd_xBi_2$ [55, 56], $CeNi_xSb_2$ [33, 34, 36], $LaNi_xSb_2$ [57, 58] etc. with low $T_c \sim < 5$ K. Although primary research work in the 112-system started to look for possible high- T_c materials, recently a large amount of work has also been performed with respect to anisotropic Dirac fermionic states [29–31, 59–64] in $(Ca/Sr)MnSb_2$ [61, 63, 65, 66], $LaAgBi_2$ [60, 67–69] and understanding their role in the observed large magnetoresistance [30, 65, 66, 68, 70, 71] and magnetothermopower generation [60, 71]. The purpose of this review article is to summarise the work done in the 112-systems so far, and to stimulate further research.

II. Synthesis Techniques

Similar to the other pnictide systems, primarily three techniques are used for bulk sample preparation of 112-pnictides [25]: (a) solid state reaction, (b) high-pressure synthesis, and (c) self-flux method. The first two methods are mostly used for polycrystalline and powder samples, while the last one is convenient for single crystal growth. Growth of single crystalline thin films by molecular beam epitaxy (MBE) is discussed in detail in Sec. VIII A.

A. Bulk Synthesis

The parent compound $CaFeAs_2$ has not yet been synthesised, but incorporation of a small amount of La in place of Ca [16, 17] was found to be essential for stabilising the 112-phase and inducing superconductivity. Single crystals of $Ca_{1-x}La_xFeAs_2$ were grown using FeAs-self-flux [16–18, 43, 49, 51] where all the constituents Ca, La, As, FeAs were mixed in appropriate stoichiometric ratio inside an aluminium crucible and sealed inside an evacuated quartz tube. In order to avoid contamination from the atmosphere, the whole process was carried out inside a glove box filled with argon gas. The sealed ampoules were heated at appropriate temperatures typically at a maximum of 1100°C and kept there for several hours. Finally the furnace was cooled slowly ($\sim 1.25^\circ\text{C}/\text{hour}$) to room temperature before taking the single crystals of maximum size of 2 mm [45] out of the furnace. Zhou *et al.* [45, 47] suggested that larger amounts of starting materials are necessary for the growth of large sized crystals and a small amount of CaO is helpful for crystallisation.

Polycrystalline samples were synthesised using solid state reaction inside a high-pressure cell [40, 48]. For

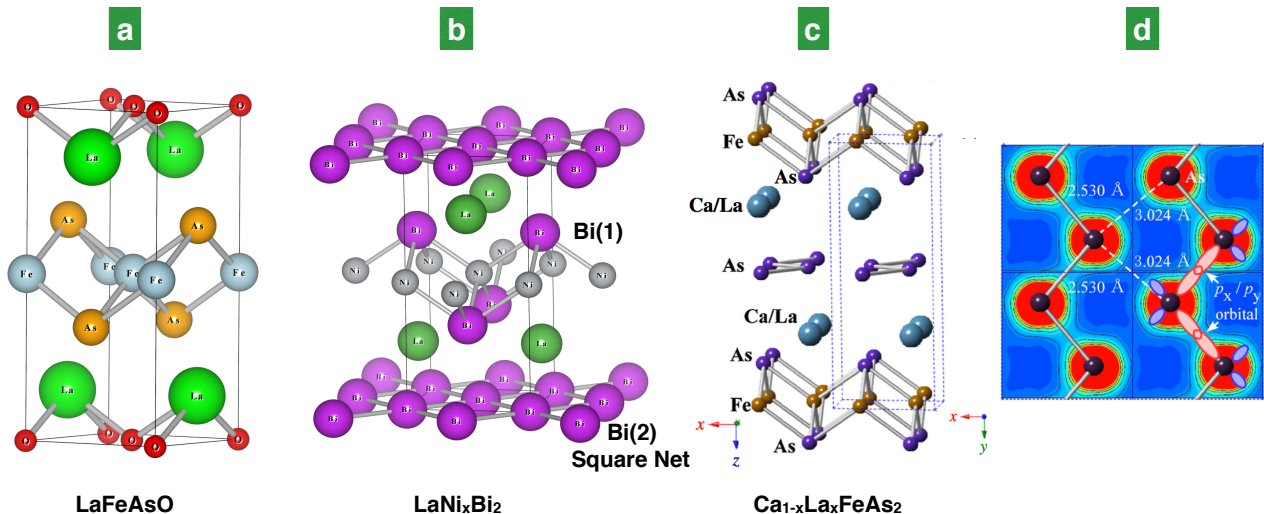


FIG. 1: Schematic crystal structures of (a) 1111-type LaFeAsO , (b) 112-type LaNi_xBi_2 and (c) 112-type $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ [16]. (d) Top view of the As-zigzag chains in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$. The colour map represents the contour of the charge distribution around As-atoms. Charge accumulation between neighbouring As-atoms are suggestive of the formation of the covalent bonds [4, 16]. [Fig. 1(c-d) : Reprinted with permission from Katayama *et al.* [16]. Copyright 2013 by the Physics Society of Japan.]

$\text{Ca}_{1-x}\text{RE}_x\text{FeAs}_2$ (RE = rare earths from La \rightarrow Gd) synthesis [48], a mixture of FeAs, REAs, Ca and As powders were mixed and pelletised which was later allowed to react inside a boron nitride crucible between 1000-1200°C for 1 h under 2 GPa pressure [42, 48, 72]. Sala *et al.* [48] pointed out that high pressure for synthesis is essential to incorporate smaller RE-ions and at much higher pressure (> 2 GPa) doping of Tb, Dy, Ho and Y into the 112-phase could be possible.

Single crystal synthesis of CeNi_xBi_2 [37], $\text{CePd}_{1-x}\text{Bi}_2$ [73], $\text{LaPd}_{1-x}\text{Bi}_2$ [56], and SrMnBi_2 [29] needed excess Bi flux and different temperature treatments while polycrystalline samples [33, 36, 38] were prepared inside an evacuated silica tube through standard solid state reaction at elevated temperatures for RENi_xBi_2 (RE = La, Ce, Nd, Y). It was observed that the Bi and Sb-based 112-systems decompose gradually when exposed to ambient atmosphere. Hence, storage of these materials in evacuated atmosphere is essential for achieving longer lifetime [33, 34, 36, 55, 57].

III. Crystal Structure

Initial reports on 112-type pnictide systems were made on RENi_xBi_2 [33] where RE = La, Ce, Nd, Gd and other rare earth elements. These 112-compounds crystallise in the HfCuSi_2 -type structure, which can be related to 1111-type compounds with the ZrCuSiAs -type structure. Structural similarity between the two phases can be found from Fig 1(a-b). The 1111-compound LaFeAsO [2] contains two different anions (O/As) while the 112-compound RENi_xBi_2 has only Bi as anion, but in two different valance states, namely Bi(1) and Bi(2).

In the stoichiometrically deficient Ni_xBi layer (analogous to the FeAs layer in LaFeAsO), Bi(1) forms a distorted tetrahedron in a trivalent charge state due to Coulomb attraction. This forces the other Bi(2) ion in a charge state of -1 to occupy a narrower space with a shorter Bi-Bi bond-length to form a square net layer as illustrated in Fig. 1(b). The presence of the two-dimensional square net layer is the most unique feature of the 112-system which stabilises due to the Coulomb attraction driven relaxation between the RE-ions. The square net layer can be considered as the blocking layer of the 112-system, though it is metallic unlike the insulating blocking layers present in other pnictide phases. The presence of the two different oxidation states of the pnictide was observed by XPS in LaPd_xSb_2 [55] where two $3d$ photoelectron lines of Sb are separated by $\Delta E = 9.4$ eV that correspond to -1 and -3 oxidation states of the Sb-atoms. A similar metallic square net layer was also observed in SrMnBi_2 (crystallizes in the SrZnBi_2 -type structure with SG $I4/mmm$ (no. 139) confirmed via neutron scattering measurements [63] as opposed to LaPd_xPn_2 with $P4/nmm$ (no. 129) symmetry) which is metallic with a large $T_N \sim 290$ K [29]. Multiple Dirac cone like dispersions were observed close to the Fermi level. In the single crystalline $\text{RENi}_x\text{Bi}_{2\pm y}$ (for R = La, Ce-Nd, Sm, Gd-Dy), a monotonic decrease in the lattice parameters a (2.1%) and c (5.3%) were observed due to the lanthanide contraction [39].

Initial reports suggests that the 112-type $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ crystallises in monoclinic structure with space group $P2_1$ (no. 4) [16] or $P2_1/m$ (no. 11) [40, 48] which is different from the other pnictide systems having

tetragonal or orthorhombic space groups. However, recently Harter *et al.*[74] observed second harmonic generation (SHG) in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ that is a signature of noncentrosymmetric crystal structure, which suggests that the space group of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ should not be centrosymmetric $\text{P2}_1/\text{m}$, but noncentrosymmetric P2_1 . The monoclinic structure stays stable up to 450 K[16]. Alternatively stacked FeAs layers are present in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ (Fig. 1(c)) separated by zig-zag As bond layers with Ca/La placed in between them [4]. The distance between neighbouring FeAs layers is slightly larger than in the 1111-phase materials. The most interesting feature of this material is the presence of 2D As layers with two different bond lengths that were measured using synchrotron X-ray diffraction [16] as shown in Fig. 1(d). The shorter one ($\sim 2.53\text{\AA}$) is identical to the As-As single bond length with As^- ($4p^4$ configuration) forming a one-dimensional zig-zag chain along the b -axis, while the larger one ($\sim 3.02\text{\AA}$) corresponds to the inter-chain distance between the zig-zag chains. In the FeAs layer, As is in a As^{3-} valance state ($4p^6$ configuration). The chemical formula of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ can be written as $(\text{Ca}_{1-x}^{2+}\text{RE}_x^{3+})(\text{Fe}^{2+}\text{As}^{3-})\text{As}^- \cdot xe^-$ with excess charge injected inside the FeAs layer [4]. This can be compared to the 1111-type CaFeAsF whose structure can be written similarly as $(\text{Ca}_{1-x}^{2+}\text{RE}_x^{3+})(\text{Fe}^{2+}\text{As}^{3-})\text{F}^- \cdot xe^-$ where F^- forms a square network. In this way, the 112- $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ structure can be related to 1111- CaFeAsF , although the chemical bondings in the spacer layers are not the same in both cases. For CaFeAsF , the CaF layer is made of strong ionic bonds while CaAs layers in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ consists of zig-zag As chains of covalent bonds weakly coupled to the adjacent Ca layers. For this reason, the interlayer distance between FeAs planes in 112- $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ ($\sim 10.35\text{\AA}$) [18] is higher than in CaFeAsF ($\sim 8.6\text{\AA}$) [75]. This layered structure was confirmed by high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) measurements of $(\text{Ca},\text{Pr})\text{FeAs}_2$ [40] with an interlayer distance of 10.4\AA . X-ray scattering data[76] suggested that microscopic manipulation of the electronically active FeAs layer is more effective compared to the larger structural tuning for controlling the superconducting properties of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$.

Recently Joseph *et al.* [44] reported the structural evolution of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ ($x = 0.18$) with temperature (110 K - 300 K) from powdered X-ray diffraction measurements. The expansion of the c -axis lattice constant goes through a distinct change around 150 K which can be correlated with a change in the resistivity slope. In this temperature range, the in-plane lattice constants go through a constant thermal expansion which is an order of magnitude smaller ($\sim 0.3 \times 10^{-4}\text{\AA}/\text{K}$) than for the c -lattice constant. The anisotropic thermal expansion suggests a change in the inter-layer interaction with temperature, although its relation to the resistivity change with temperature is not clear yet.

Alternative claims have been made that instead of

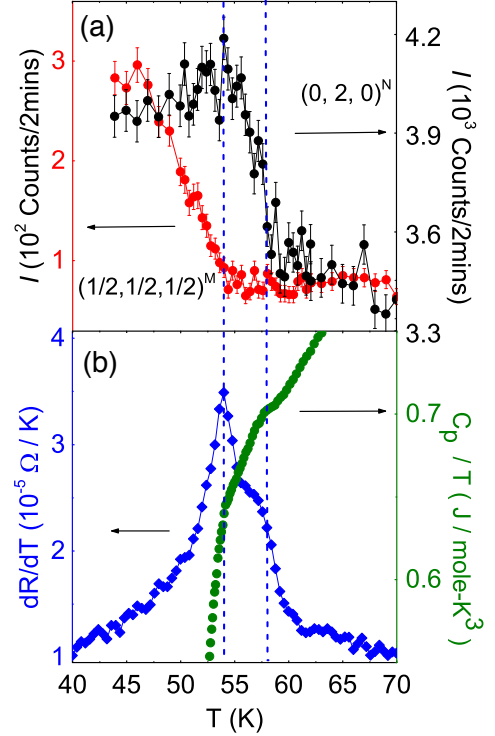


FIG. 2: Temperature dependence of the (a) neutron intensity of nuclear $(0\ 2\ 0)^N$ and magnetic $(1/2\ 1/2\ 1/2)^M$ peaks, (b) Specific heat (C_p) and derivative of the in-plane resistivity ($\rho \parallel ab$) in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$. The dotted lines are the temperatures at which the structural resp. magnetic phase transitions were observed[54]. Reprinted with permission from Jiang *et al.*[54]. Copyright 2015 by American Physical Society.

CaFeAs_2 [28], $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ ($x = 0.27$)[54, 74] is the non-superconducting parent compound of this family which is naturally structurally detwinned at ambient pressure and becomes superconducting on electron or hole-doping. Neutron diffraction and muon spin rotation (μSR) measurements suggested a structural phase transition from a monoclinic to a triclinic phase at 58 K and a paramagnetic to stripe AFM phase transition at 54 K (Fig. 2), both of which can be suppressed by Co-substitution on the Fe-sites[54]. Additionally, the presence of two different crystallographic phases in different temperature regions were further confirmed from an optical 2^{nd} harmonic generation study[74] where no significant modification of the electronic structure was observed as a result of the phase transitions. A similar structural phase transition was recently reported in superconducting $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ ($x = 0.15$) around 100 K using temperature dependent X-ray measurements[77] while Kawasaki *et al.*[51] reported an AFM ordering around $T_N \sim 62\text{ K}$ for a sample with bulk $T_c \sim 35\text{ K}$. This suggests a correlation between the structural and AFM phase transition in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ occurring in similar

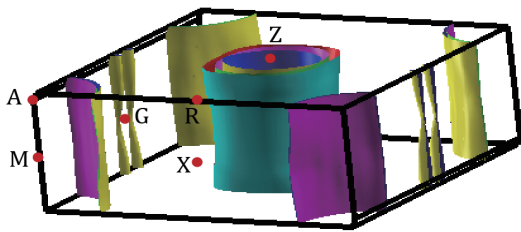


FIG. 3: DFT calculated Fermi surface of CaFeAs_2 in the non-magnetic state[53]. Reprinted with permission from Huang *et al.*[53]. Copyright 2015 by American Institute of Physics.

temperature window and a weak coupling between the structural and magnetic order.

Upon Co-doping into $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ ($x = 0.2$) [49], a mixture of 112- and 122-phases were observed. For low Co-content, almost pure 112-phase was found with monoclinic structure, but with an enhancement of the Co-doping level a mixture of the 112 and 122-phases were observed which for a higher Co-doping ($> 6\%$) resulted even in the complete disappearance of the 112-phase. Owing to the slightly smaller ionic radius of Co^{2+} (74 pm) compared to Fe^{2+} (76 pm), the successful substitution could be confirmed from the shift of the out-of-plane X-ray reflection. This suggests that the structural stability of the 112-phase only exists in a narrow window of Co-doping level putting strong constraints to the crystal growth conditions.

IV. Electronic Structure

A. Theoretical Investigations

Density functional theory (DFT) band structure analysis of fully stoichiometric LaPdBi_2 revealed the almost equal contribution of all constituent atoms near the Fermi level, except for Pd which has a much higher dominance. Changing the Pd content in CePd_xBi_2 affects the Fermi surface topology significantly and in the presence of significant Pd vacancies, Fermi surface nesting can be avoided. This suppresses any kind of charge density wave (CDW) in the Bi square net layer which allows the superconducting state to stabilise[56].

The density of states of two hypothetical 112-structures BaFeAs_2 and BaFeSb_2 [28] showed a considerable amount of Fe-3d states at E_F with a small contribution from the spacer layer. This has been claimed to originate from the larger distance of separation between the As(1) and FeAs layers with minimal hybridisation between them. For CaFeAs_2 , first-principles calculation also suggested the strong presence of Fe-3d electrons in the density of states near the Fermi level [16, 53]. The Fermi surface of CaFeAs_2 consists of two electron cylinders at the Brillouin zone (BZ) corner (M point), four Dirac cone type electron cones at the BZ edge (G point) and three hole cylinders with an additional

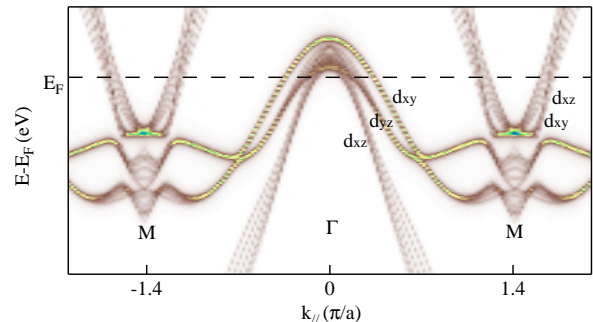


FIG. 4: Band structure of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ projected to the in-plane BZ as obtained from ARPES measurements[52]. Reprinted with permission from Liu *et al.*[52]. Copyright 2015 by American Institute of Physics.

three-dimensional (3D) hole pocket at the BZ centre (Γ point)[16, 53, 78, 79] as illustrated in Fig. 3. The presence of the additional hole pocket at $(0,0,0)$ (likely originating from the hybridisation between the Fe $3d_{xz}/3d_{yz}$ and As(1) $4p$ orbitals from the FeAs layer) and four electron cones at the G point (contributed by As(2) p -states) have not been found earlier in 1111[80, 81] and 122[82]-pnictide phases. The nesting between the Γ point hole pockets and G point electron cones possibly results into a AFM spin density wave (SDW) phase which gets suppressed upon RE -doping favoring the superconducting state[53, 83].

The band dispersion in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ showed considerable 2D character contributed mostly by the As layers. In the non-magnetic calculation, four hole-like bands (around $\Gamma(0,0)$ point) and two electron-like bands (around $M(\pi,\pi)$ point) were found from the band structure analysis (see Fig. 4) which has some similarity with BaFe_2As_2 [78]. It was predicted that for $T < T_c$, $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ could work as a natural topological insulator/superconductor hybrid structure (FeAs layer to be responsible for the superconductivity and the As chain layer being the topological insulator) that could be ideal for the realisation of Majorana fermions[84].

Nagai *et al.* [85] investigated the effect of Sb-substitution on the superconducting properties of $\text{CaFe}(\text{Sb}_x\text{As}_{1-x})_2$. Sb-doping in the As zig-zag layer increased the lattice parameters a, b with an overall increase in the unit cell volume leading to an overall stabilisation of the structure which is energetically more favourable than substitution in the FeAs layer. However, the calculated band structure with and without Sb-doping is very similar except a small shift along the $G-\Gamma$ direction. Primary investigations suggested the role of Sb-substitution in the enhancement of T_c to be possibly related to the stabilisation of the As-chains which have a crucial role in controlling T_c .

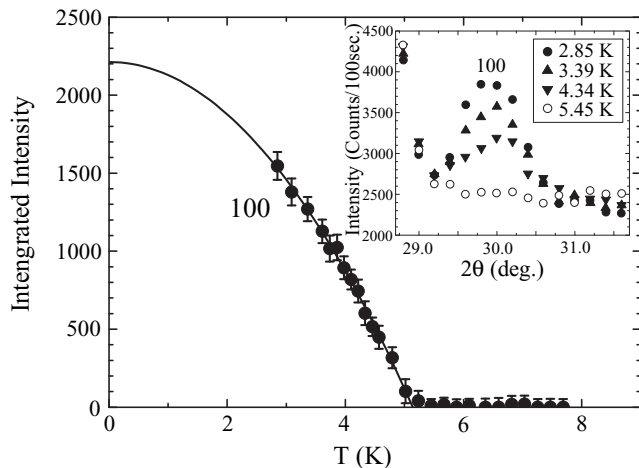


FIG. 5: Temperature dependence of the integrated intensity of the (100) Bragg peak as obtained from neutron diffraction measurements of CeNi_xBi_2 . The solid line describes a $(1 - (T/T_N)^2)$ dependence of the intensity below 5 K[36]. Reprinted with permission from Kodama *et al.*[36]. Copyright 2011 by American Physical Society.

B. Experimental Results

ARPES measurements on $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ indicated a band structure similar to the other pnictide systems consisting of three hole like bands (d_{xz}, d_{yz}, d_{xy} character) at the Γ point and two electron like bands (d_{xz}, d_{xy} types) at the M point of the BZ[50, 52, 54, 78], with reasonable nesting mostly originating from the Fe-3d electrons (see Fig. 4). No evidence of the As- p or Ca- d states were found in the Fermi surface map scanned over a complete 3D momentum space which is similar to the absence of interstitial blocks on the Fermi surface in 1038-phase $(\text{CaFeAs})_{10}\text{Pt}_{3.58}\text{As}_8$ and 1048-phase $(\text{CaFe}_{0.95}\text{Pt}_{0.05}\text{As})_{10}\text{Pt}_3\text{As}_8$ [86] and 1111-phase $\text{SmFe}_{1-x}\text{Co}_x\text{AsO}$ [87] systems, but in contrast to the predictions made from electronic structure calculations[83]. However, Li *et al.*[50] managed to resolve the presence of an additional 3D hole like band at the zone centre and a fast disappearing band near the X-point at the zone corner in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ ($x=0.1$) and also for $x = 0.27$ [54]. The presence of a considerable As-4 p_z orbital for the hole like band and As-4 $p_{x,y}$ orbitals for the narrow band were resolved while considerable hybridisation between the As-4 p_z and Fe-3d orbitals were found in the hole-like band.

V. Magnetic Structure

The layered compound CePd_xBi_2 is a Kondo-lattice AFM which is metallic above 75 K, and exhibits below 75 K a strong interplay between Kondo and crystal field effects (CEF)[73]. Magnetic susceptibility data suggested that the material is anisotropic due to the CEF effects with an AFM ordering temperature $T_N = 6$ K[56]. The high-temperature susceptibility fitted using the Curie-

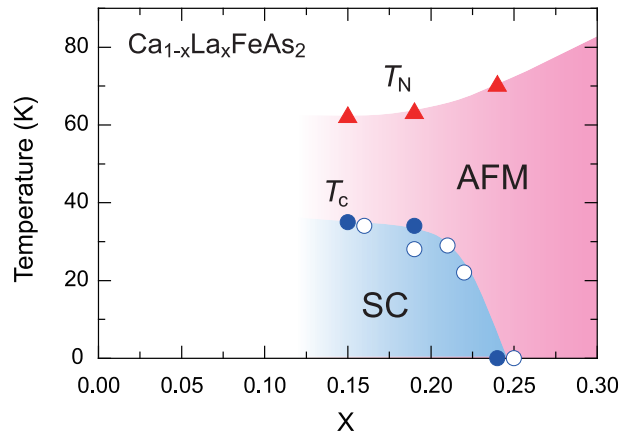


FIG. 6: Phase diagram of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ for various doping levels of La[51]. Reprinted with permission from Kawasaki *et al.*[51]. Copyright 2015 by American Physical Society.

Weiss law $\chi = C/(T - \theta_c)$ revealed a Curie Temperature $\theta_c = -1.5$ K and an effective magnetic moment $\mu_{\text{eff}} = 2.86\mu_B/\text{Ce}$ atom which is of similar value as for a free Ce^{3+} ion indicating the localised nature of the Ce-moments in CePd_xBi_2 . The negative θ_c supports the existence of AFM ordering of the Ce-atoms at higher temperatures[56]. The Hall-coefficient R_H of CePd_xBi_2 is negative with an average value of $1.7 \times 10^{-4} \text{ cm}^3/\text{C}$ which corresponds to a carrier concentration of $3.7 \times 10^{22}/\text{cm}^3$. R_H stays temperature independent suggesting a single-band character of the carriers [56]. The strong interplay between the Kondo and CEF interactions leads to a reconstruction of the Fermi surface topology which is most likely responsible for the absence of superconductivity in CePd_xBi_2 as iso-structural LaPd_xBi_2 is superconducting and both have similar Fermi surfaces above 75 K. Electronic structure calculation suggested that the Pd-vacancies induce strong scattering effects in the Pd_xBi layer that enhances the CEF effect to quench the Ce moments at low temperature. The Fermi surface reconstruction and Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction induced magnetic ordering can induce superconductivity in the heavy-fermion system CeCu_2Si_2 [88], which is unlikely to occur in the case of CePd_xBi_2 without external influences[73].

The ground state of the Ce-based intermetallic compound CeNi_xBi_2 is governed by the interplay between RKKY and Kondo interactions. The Kondo interaction strength is determined by the level of hybridisation between the Ce-4f and conduction electrons favoring a non-magnetic ground state while the long range magnetically ordered state is preferred by the RKKY interaction[39]. The parent compound of CeNi_xBi_2 is CeNiBi_2 which is a moderately heavy-fermion antiferromagnet with a magnetic ordering temperature T_N of 5 K[36]. Rosa *et al.*[32] reported that T_N in $\text{CeNi}_x\text{Bi}_{2-y}$ increases with an increase in x , which also enhances the magnetic anisotropy of Ce^{3+} at low temperature. Below 5 K, the Ce moments

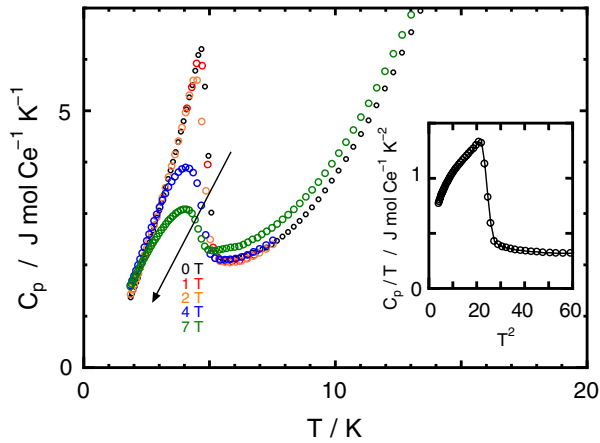


FIG. 7: Temperature dependence of the specific heat (C_p) for different applied magnetic fields with distinct λ peak around 5 K in CeNi_xBi_2 . Inset: $C_p/T - T^2$ at 0 Oe[33]. Reprinted with permission from Mizoguchi *et al.*[33]. Copyright 2011 by American Physical Society.

order antiferromagnetically with the easy magnetisation axis along the c -direction with a saturated magnetic moment of $1.71\mu_B$ as $T \rightarrow 0$ K. Superconductivity is induced in CeNiBi_2 via Ni-deficiency similar to the oxygen deficiency in the 1111-system[89]. From powder neutron diffraction measurements (see Fig. 5) clear Bragg peaks are observed at $q = (0, 0, 0)$ below the magnetic ordering temperature $T_N \sim 5.45$ K and the intensity of the (100) Bragg peak increases down to the lowest temperature. However, no anomaly or jump was observed in the peak intensity around T_c which is unlike the features observed in heavy-fermion superconductors where Bragg intensities are suppressed below T_c [90]. This suggested that Ce-4*f* electrons do not contribute to the superconductivity and the material cannot be considered to be a heavy-fermion superconductor. Although CeNi_xBi_2 has a similar crystal structure like 1111-pnictide, the T_c is much lower than in the 1111-system which can be due to the absence of magnetic fluctuations in CeNi_xBi_2 [36]. Anisotropic magnetic behavior was observed in the single crystalline $RE\text{Ni}_x\text{Bi}_{2\pm y}$ compounds ($RE = \text{Ce-Nd, Sm, Gd-Dy}$) which order antiferromagnetically at low temperatures between 3.3 K (Sm) and 10.2 K (Tb)[39].

From first-principles based investigation, the ground state of CaFeAs_2 was predicted to be a SDW type striped AFM phase driven by Fermi surface nesting with the magnetic moment of each Fe atom to be $2.1\mu_B$ [53], significantly smaller in value than the LDA calculated value for 1111- LaFeAsO [16] and the hypothetical 112-compounds BaFeAs_2 and BaFeSb_2 [28]. Electron doping using rare-earth elements can help suppressing the SDW state and stabilising the superconducting state. Nuclear magnetic resonance (NMR) measurements revealed that the AFM ordering sets in below $T_N = 62$ K for highly doped $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ ($x = 0.15$) while superconductiv-

ity sets in at $T_c = 35$ K [51]. With an increase in the doping concentration, AFM order gets enhanced as T_N rising up to 70 K[51] for $x = 0.24$ (see Fig. 6) which possibly originates from the nesting of the Fermi surfaces due to additional electron doping by La[50, 78]. The AFM order in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ has been found to be robust against RE doping. A similar phase diagram was also obtained for the 1111-system $\text{LaFeAsO}_{1-x}\text{H}_x$ [91, 92] where heavy doping enhanced T_N and, in both cases, a structural phase transition was observed above T_N [54, 92]. However, the superconducting and AFM orders coexist in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ microscopically[51], while both orders are completely segregated in $\text{LaFeAsO}_{1-x}\text{H}_x$ [93].

VI. Superconducting Properties

A. Low Critical Temperature Materials

CeNi_xBi_2 is a type-II superconductor ($T_c = 4.2$ K)[33] with a SVF of 96%. Below 10 K, the resistivity shows a $\rho(T) \sim T^2$ dependence and increases linearly with temperature up to 100 K. For other RE -containing $RE\text{Ni}_x\text{Bi}_2$ systems with $RE = \text{La, Nd, Y}$, also T_c values around 4 K were measured, but the SVF was significantly less than the Ce-containing phase. The specific heat data for CeNi_xBi_2 (see Fig. 7) suggested the presence of two different types of carriers with different effective masses. The AFM ordering around 5 K was caused by the heavy carriers originating from the magnetic interaction between conduction electrons and Ce-4*f* electrons in the Ni_xBi plane, while the light carriers from the Bi square net layer were responsible for superconductivity. The entropy calculation suggested that the sharp jump in the specific heat around T_c corresponds to the magnetic ordering of Ce-4*f* moments, which are not involved in the occurrence of superconductivity. Lin *et al.*[39] claimed that the observed superconducting properties of LaNi_xBi_2 and CeNi_xBi_2 are most likely due to the presence of Bi and Ni-Bi binary impurities as very little evidence of bulk superconductivity was found from their single crystalline samples. However, highly crystalline thin films also showed superconductivity around 4 K[34, 55]. The zero-resistance state in LaPd_xBi_2 [56] was observed around 2 K with a bulk superconducting phase around the same temperature which is likely s -wave in nature. In the normal state, it is metallic with a residual resistivity ratio (RRR) of 2.45 indicating strong scattering in the conducting layers.

B. High Critical Temperature Materials

1. Rare Earth Substitution

The predicted mother compound of the (Ca, RE) -112 family CaFeAs_2 has not been synthesised yet and superconductivity was only observed in the RE -doped systems within a limited doping range. Doping of RE -elements also improved the T_c value of 122-type $(\text{Ca}, RE)\text{Fe}_2\text{As}_2$ with T_c^{onset} values : $\text{Ca}_{1-x}\text{Pr}_x\text{Fe}_2\text{As}_2$ (47 K)[94],

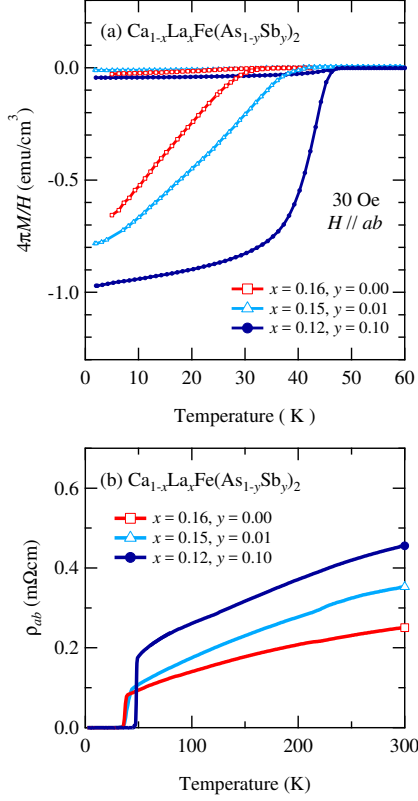


FIG. 8: Temperature dependence of the (a) magnetisation at $H(\parallel ab) = 30$ G in ZFC and FC conditions and (b) in-plane resistivity ($\rho \parallel ab$) for different La and Sb-doping in $\text{Ca}_{1-x}\text{La}_x\text{Fe}(\text{As}_{1-y}\text{Sb}_y)_2$ [18]. Reprinted with permission from Kudo *et al.* [18]. Copyright 2014 by Physics Society of Japan.

$\text{Ca}_{1-x}\text{La}_x\text{Fe}_2(\text{As}_{1-y}\text{P}_y)_2$ (45K) [95], $\text{Ca}_{1-x}\text{Pr}_x\text{Fe}_2\text{As}_2$ (49K) [96]. However, complete appearance of bulk superconductivity was not observed in some of these cases, possibly relating to the filamentary nature of the superconducting phase.

The in-plane resistivity of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ with $x = 0.16$ goes through a superconducting transition at 36 K [16] with a transition width of 2.4 K and bulk superconductivity was observed from magnetisation measurements at 34 K with a SVF of 66%. For $x = 0.21$, T_c^{onset} increased to 45 K [16], but the zero-resistance state was only observed at 25 K which is consistent with the T_c determined from the magnetisation data. In $(\text{Ca}_{0.9}\text{Pr}_{0.1})\text{Fe}_{1.3}\text{As}_{1.8}\text{O}_{0.2}$, a small level of O-doping helped enhancing the SVF as bulk superconductivity was observed with a T_c of 20 K [40].

Replacing As by a small amount of isovalent substitutional elements like P and Sb enhanced T_c further [17]. For 5% P doping in $\text{Ca}_{1-x}\text{La}_x\text{Fe}(\text{As}_{0.995}\text{P}_{0.005})_2$ ($x = 0.16$) bulk T_c was enhanced to 41 K with a SVF of 44% at 5 K. For $x = 0.18$, T_c got reduced to

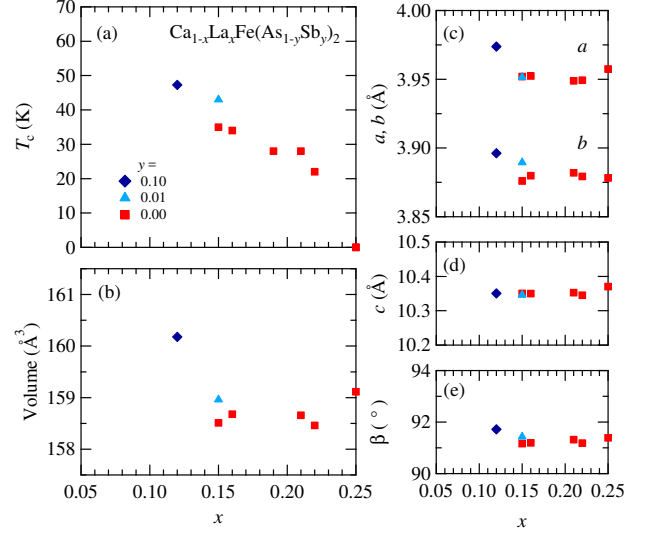


FIG. 9: Dependence of (a) T_c , (b) unit cell volume, (c) a , b lattice constants, (d) c -lattice constant, and (e) β angle of $\text{Ca}_{1-x}\text{La}_x\text{Fe}(\text{As}_{1-y}\text{Sb}_y)_2$ for various La-doping levels x . [18]. Reprinted with permission from Kudo *et al.* [18]. Copyright 2014 by Physics Society of Japan.

39 K, but the SVF increased to 77%. For Sb-doped $\text{Ca}_{1-x}\text{La}_x\text{Fe}(\text{As}_{0.99}\text{Sb}_{0.01})_2$ ($x = 0.16$), the bulk T_c increased to 43 K with a significant SVF of 78%. From the trend in the T_c vs. x phase diagram in Fig. 9(a), the highest T_c was found for all materials at the lowest x value. This suggests that a much higher T_c could be expected if x can be reduced further below 0.15 which needs development of chemical synthesis techniques.

Further enhancement of T_c was possible with a higher level of Sb substitution in $\text{Ca}_{1-x}\text{La}_x\text{Fe}(\text{As}_{1-y}\text{Sb}_y)_2$ ($x = 0.12, y = 0.1$) to 47 K [18] with a SVF of 100% at 2 K (see Fig. 8) indicating the appearance of complete bulk superconductivity. This enhanced T_c could originate from two different effects: (1) simultaneous Sb doping, (2) decrease in La content resulting in an increase in cell volume (Fig. 9(b)). The decrease in La content suggests the reduction of the number of charge carriers as the ionic radii of La^{3+} and Ca^{2+} are comparable. Secondly, additional Sb substitution can induce a negative chemical pressure due to an increase in cell volume as the ionic radius of Sb^{3-} (Sb^-) is larger than As^{3-} (As^-) which was observed from the increase in the a, b lattice constants (see Fig. 9(c-d)) and the higher level of localisation of the d -electrons with a larger sized Pn atom. However, this mechanism is not valid for the T_c enhancement in the P-doped system [17] as neither the La content got reduced nor the lattice parameters changed in that case.

In Sb-substituted $\text{Ca}_{1-x}\text{RE}_x\text{Fe}(\text{As}_{1-y}\text{Sb}_y)_2$, there is a general trend of T_c enhancement and improvement of the superconducting properties [18]. In the absence of Sb ($y = 0$), for the Ce-doped system, no evidence of bulk superconductivity was observed, while Pr- and Nd-doped

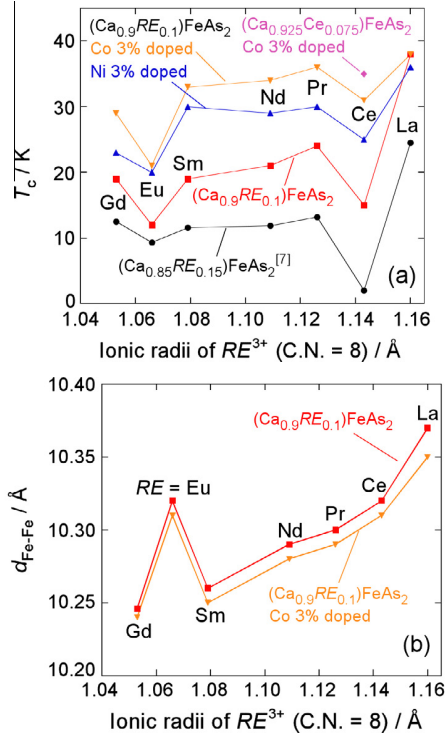


FIG. 10: (a) T_c and (b) d_{Fe-Fe} of $(Ca,RE)FeAs_2$ as function of the ionic radii of various RE^{3+} ions with coordination number eight[42]. Reprinted with permission from Yakita *et al.*[42]. Copyright 2015 by Elsevier.

systems exhibited T_c at 10 K and 11 K respectively with a SVF of 5%. For the Ce-doped system, the origin of the zero-resistance state was attributed to filamentary superconductivity as no clear diamagnetic signal was observed at T_c . Sb-doping improved superconductivity with a T_c of 21 K ($y = 0.01$) and 43 K ($y = 0.1$) for the Ce-doped system, 26 K ($y = 0.01$) and 43 K ($y = 0.05$) for the Pr-doped system, 24 K ($y = 0.01$) and 43 K ($y = 0.05$) for the Nd-doped systems with a substantial increase in the SVF indicating the appearance of bulk superconductivity in all these phases. This suggests that irrespective of the RE element, a T_c above 40 K can be obtained by tuning the Sb content. Due to Sb substitution, the b -lattice parameter increased which helped enhancing T_c , but the c -value stayed almost unchanged for $x = 0.15 - 0.25$ (see Fig. 9(c-e)). Kudo *et al.* [18] suggested that T_c can be increased beyond 50 K if the b -lattice constant becomes equal to a with a simultaneous reduction of the c -value to adjust the As-Fe-As bond angle.

In polycrystalline $Ca_{1-x}RE_xFeAs_2$, superconductivity was observed with a T_c of 22.7 K, 24.6 K, 17.9 K, 23.2 K, 13.2 K and 22.8 K for La-, Pr-, Nd-, Sm-, Eu- and Gd-doped systems respectively, except for the Ce-doped system[48]. Broad resistive transitions were observed due to the inhomogeneous distribution of the RE atoms resulting in poor grain connectivity in the polycrystalline phases. There is an indication of a decrease

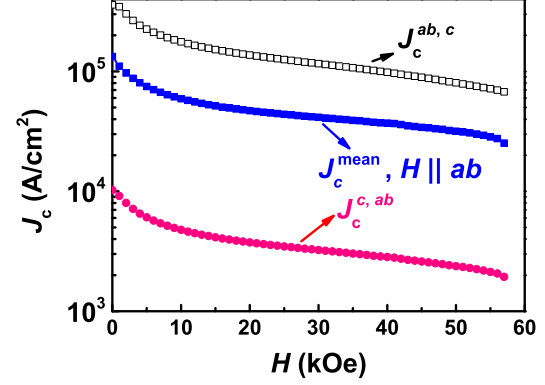


FIG. 11: Magnetic field dependence of critical current density J_c of $Ca_{1-x}La_xFeAs_2$ in the in-plane ($H \parallel ab$) and out-of-plane ($H \parallel c$) configuration[47]. Reprinted with permission from Zhou *et al.*[47]. Copyright 2014 by Japanese Society of Applied Physics.

of T_c with decrease of the ionic radii of the RE atoms, a similar behavior was observed for d_{Fe-Fe} (interlayer distance between the neighbouring Fe planes). Note that none of these trends are clearly established due to the inhomogeneity of the phases. Compositional analysis revealed that the actual level of Ce in the Ca site is high due to the similar ionic radii [42] which could be a reason behind the absence of superconductivity in the Ce-doped system.

2. Transition Metal Substitution

In the RE -substituted material $Ca_{1-x}RE_xFeAs_2$, transition metal (TM)-co-doping indicates the direct substitution of the Fe atoms by Co-atoms which has been studied for $TM = Co, Ni, Mn$ [42, 49, 72]. Mn-co-doping suppressed superconductivity completely. However, it was found that a small level (3%) of Co- and Ni-doping improved the superconducting properties of the $(Ca,RE)112$ -systems[42, 49]. Co-co-doped $Ca_{1-x}RE_x(Fe_{1-y}Co_y)As_2$ has an enhanced T_c above 30 K for $RE = La, Ce, Pr, Nd, Sm$, in spite of the direct TM substitution on the Fe-sites. This effect is similar for Ni-doped systems with slightly lower T_c compared to the Co-doped phases suggesting an overdoped state of the Ni-doped systems. On 3% Co-co-doping, the T_c of the (Ca,Pr) -112 system increased significantly from 23 K (TM -free case) to 36 K[72], while also the superconducting transition became sharper suggesting improved grain connectivity with significant enhancement in the T_c^{zero} value (from 14 K \rightarrow 30 K) and no change in the T_c^{onset} value. With an increase in the Co-doping level, a linear suppression of T_c^{zero} and T_c^{onset} was observed at an average rate of 1.65 K/Co%[49].

Large diamagnetic screening was observed in the Co-co-doped (Ca, La) -112-system indicating the presence of bulk superconductivity[42], although it was not clear why a direct substitution of Co for Fe would result in

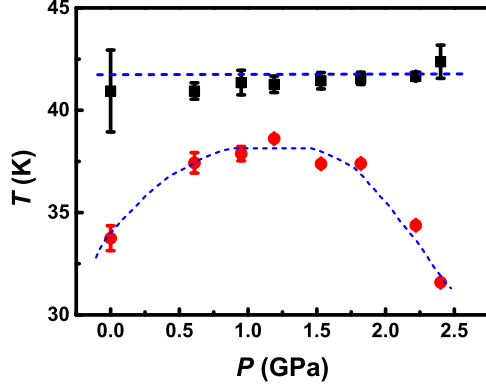


FIG. 12: Pressure dependence of T_1 and T_c^{zero} of $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ with $x = 0.18$ single crystals[45]. Reprinted with permission from Zhou *et al.*[45]. Copyright 2015 by Institute of Physics.

such behavior which is also contrary to doping effects in 122- and 1111-phases [97, 98]. However, the improved superconducting properties could arise from the decrease in La-content in the Co-doped phases, similar to Sb doping in (Ca,La)-112[18] which resulted in an optimisation of the As-Fe-As bond angle.

In $\text{Ca}_{1-x}\text{RE}_x(\text{Fe}_{1-y}\text{TM}_y)\text{As}_2$ ($\text{TM} = \text{Co, Ni}$), T_c increased with increasing ionic radii for all RE elements except for Ce and Eu. $d_{\text{Fe-Fe}}$ went through a similar trend with ionic radii which is comparable to the trend observed earlier in the TM-free (Ca,RE)112-system[48] (see Fig. 10). Co-co-doping resulted in slight reduction of $d_{\text{Fe-Fe}}$ for all (Ca, RE)112-systems, keeping the $d_{\text{Fe-Fe}}$ vs ionic radii trend the same for Co-free and Co-doped cases. For the (Ca,Ce)112-system, the reduction of the Ce-content increased the T_c and with Co-co-doping followed the same trend. For the Eu-doped system, an exceptionally low T_c and large $d_{\text{Fe-Fe}}$ was measured which most likely indicates the coexistence of Eu^{2+} and Eu^{3+} .

3. Critical Current and Critical Field

The lower critical fields (H_{c1}) for CeNi_xBi_2 , LaNi_xBi_2 , NdNi_xBi_2 , YNi_xBi_2 are 65 G, 90 G, 55 G and 67 G respectively [33]. The upper critical fields (H_{c2}) at zero-temperature for LaPd_xBi_2 was 3 T [56] which is relatively large for a $T_c \sim 2$ K suggesting type-II superconductivity. For $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$, critical fields near $T = 0$ are as high as $H_{c2}^c(0) = 39.4$ T (for $H \parallel c$) and $H_{c2}^{ab}(0) = 166.2$ T (for $H \parallel ab$) which corresponds to coherence lengths[47, 77] of $\xi_c(0) = 6.9$ Å and $\xi_{ab}(0) = 28.9$ Å. The anisotropy $\gamma(0)$ near T_c is 2.8 which lies in between 1111 ($5 < \gamma < 9.2$)[99]- and 122 ($1 < \gamma < 2$)[100]-type pnictides. γ is a measure of the interlayer coupling strength between the FeAs and charge reservoir layers suggesting the presence of moderate anisotropy in 112-system. The anisotropic pinning potential in $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ showed a field dependence for $H \parallel ab$ similar to the cuprates and the 1111-system[99] suggest-

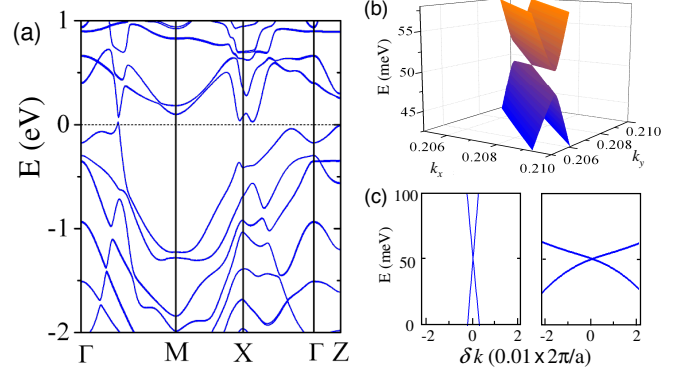


FIG. 13: (a) Electronic band structure of SrMnBi_2 . (b) Anisotropic energy surfaces around the Dirac point $k_0 = (0.208, 0.208)$ for the $(\text{SrBi})^+$ layer in SrMnBi_2 . (c) Energy dispersions near the Dirac point along parallel and perpendicular directions to the $\Gamma - M$ symmetry line in SrMnBi_2 [31]. Reprinted with permission from Park *et al.*[31]. Copyright 2011 by American Physics Society.

ing a transition from single-vortex dominated pinning to a small bundle pinning. This indicates a relatively 2D nature of the superconducting state as that in the 122-system[47]. The critical current density J_c for 112- $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ is about $\sim 10^5$ A/cm² (see Fig. 11), only weakly dependent on the direction and strength of the applied magnetic field[47, 77]. However, in Sb-doped $\text{Ca}_{0.85}\text{La}_{0.15}\text{Fe}(\text{As}_{0.92}\text{Sb}_{0.08})_2$, significant improvement in the J_c value[101] was measured ($\sim 2.2 \times 10^6$ A/cm²), which upon high energy proton irradiation can be enhanced upto a value of 6.2×10^6 A/cm². The J_c value is comparable to that of 11-type $\text{Fe}_{1+y}(\text{Te,Se})$ [102] suggesting the importance of strong bulk-dominated or artificial defect induced pinning in enhancing the value of J_c .

4. Effect of Pressure

Application of external pressure can be useful for the suppression of the AFM ground state and stabilisation of superconductivity in Fe-based superconductors without introducing substitutional elements or impurities. For $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$, Zhou *et al.* [45] observed that the resistivity went through a two-step decrease with temperature towards the superconducting phase while no effect of pressure was observed on the normal state resistivity. The temperature (T_1) at which the high- T resistance decrease took place was found to be pressure independent. Both the T_c^{onset} and T_c^{zero} indicated a dome-shaped pressure dependence with its maximum at around 1.19 GPa as illustrated in Fig. 12. The pressure coefficients were comparable to that of other pnictide phases [103, 104]. The maximum T_c^{zero} was 38.5 K at 1.19 GPa which is much higher than the zero-pressure value of 34 K, suggesting that the enhancement of T_c is possible further in the doped 112-compounds via tuning of the As-Fe-As bond angle as result of the Sb substitution.

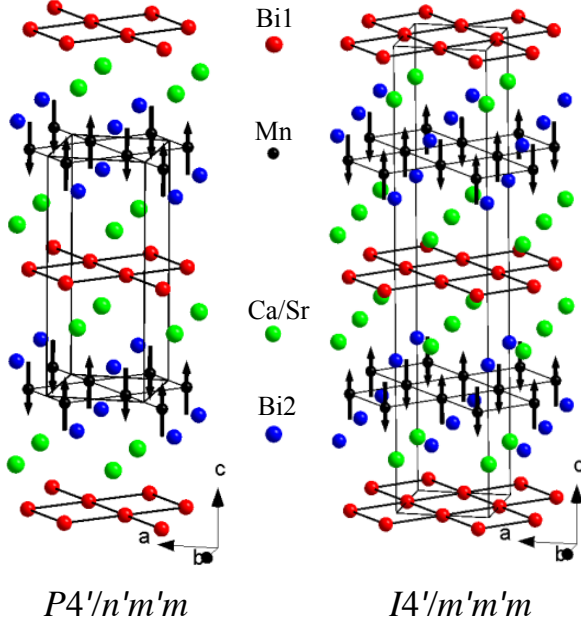


FIG. 14: Ground state magnetic configurations of CaMnBi_2 (left) and SrMnBi_2 (right)[63]. Reprinted with permission from Guo *et al.*[63]. Copyright 2014 by American Physics Society.

VII. Dirac Fermions

Dirac materials like graphene[105] and topological insulators[106] have attracted significant research interest recently due to their novel quantum mechanical properties that could be useful for quantum computation, nanoelectronics and spintronics. The linear energy dispersion in these materials is governed by the relativistic Dirac equation and the crossing of the linearly dispersed bands at the Dirac point forming a Dirac cone[63]. This configuration suppresses carrier backscattering and enhances electron mobility[31] resulting in novel quantum phenomena like anomalous quantum hall effect and a non-zero Berry phase[105, 106]. The linear energy dispersion also results in large magnetoresistance which increases linearly with magnetic field and does not saturate at higher field[30, 65, 66, 68, 70, 71] as the lowest Landau level can be easily accessed by the Dirac fermions in the quantum limit at moderate applied field. Unlike graphene[105], topological insulators[106] and d -wave superconductors[63] with isotropic Dirac cone structures, the range of Dirac materials can be extended further by introducing anisotropy in the Dirac cone for making new electronic devices where electron propagation will be different in different directions from the Dirac point. While various approaches like coupled heterostructures[107], application of strain[108] etc. have been proposed to generate anisotropy[64] in Dirac materials, layered intermetallic compounds like SrMnBi_2 [29–31, 59–64], CaMnBi_2 [61, 63, 65, 66], LaAgBi_2 [60, 67–69] with 112-pnictide structures naturally contain anisotropic Dirac cones (see Fig. 13). The Bi square net layers host the Dirac fermions in such compounds, and the linear en-

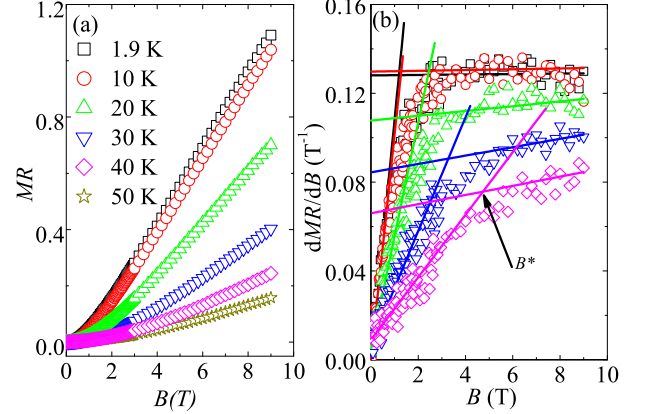


FIG. 15: (a) The magnetic field dependence of the in-plane $MR = (\rho(B) - \rho(0))/\rho(0)$ at various temperatures. (b) First derivative of MR ($d(MR)/dB$) as function of applied magnetic field at different temperatures. Data at high field was fitted by $MR \sim f(B) + f(B^2)$ and at low field by $MR \sim f(B^2)$ [30]. Reprinted with permission from Wang *et al.*[30]. Copyright 2011 by American Physics Society.

ergy dispersion originates from the crossing of the two $\text{Bi-}6p_{x,y}$ bands[31] which has also been supported by first-principles calculations[68] and tight-binding analysis[61]. The tetragonal unit cell of these materials (space group $I4/mmm$) is constituted by $\text{Mn-Bi}_{(2)}$ layers (analogous to the FePn layers) which are separated by $\text{Sr/Bi}_{(1)}$ layers (Fig. 14) on both sides with the c -axis length larger than in other pnictide superconductors[28, 29]. Bi exists in two different valance states in the blocking and tetrahedral layers which is common for 112-phase pnictides.

ARPES measurements on SrMnBi_2 [31] revealed the presence of a large circular Fermi surface at the zone centre (Γ -point) and a needle-like Fermi surface between the Γ and M point, as also predicted theoretically. Dirac type dispersion was observed from the needle-shaped Fermi surface along the $\Gamma - M$ line along which the estimated Fermi velocity ($v_F^{\parallel} = 1.51 \times 10^6$ m/s (comparable to that of graphene[105]), while the velocity perpendicular to the $\Gamma - M$ direction (v_F^{\perp}) is $\sim 1.91 \times 10^5$ m/s. The resulting anisotropy in v_F along different directions of the Dirac cone is $v_F^{\parallel}/v_F^{\perp} \geq 5$, in agreement with theoretical predictions[31, 62]. Such anisotropy has been claimed to originate from the different levels of hybridisations in different directions, which along the $\Gamma - M$ line is determined by the overlap between neighbouring Bi atoms in the square net layer, and in the perpendicular direction is determined by the hybridisation strength between the $\text{Sr-}d_{xy,yz}$ and $\text{Bi-}p_{x,y}$ orbitals. Jo *et al.*[59] demonstrated that the interlayer conduction in SrMnBi_2 can be valley-polarised under the presence of a tilted magnetic field which also enhances the anisotropy significantly (~ 100) at high magnetic field.

Unlike graphene with a negligible spin-orbit coupled

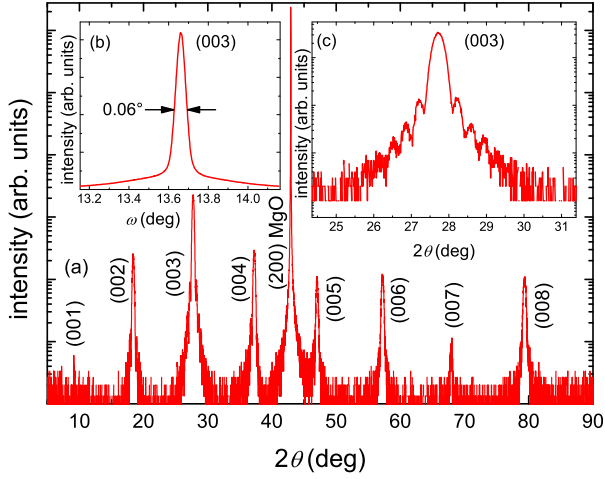


FIG. 16: (a) Out-of-plane ($2\theta - \omega$) XRD scans of LaNi_xBi_2 grown on a $\text{MgO}(100)$ substrate. (b) Typical rocking curve of the (003) peak. (c) Zoom of the (003) peak with Laue fringes[57]. Reprinted with permission from Buckow *et al.*[57] Copyright 2013 by Institute of Physics.

(SOC) band gap[109], the SOC gap for SrMnBi_2 is ~ 40 meV at the Dirac point which can produce a large spin-hall effect[31]. The small effective mass ($0.29m_e$), relatively larger carrier mobility ($250\text{ cm}^2/\text{Vs}$) and small Fermi surface volume support the existence of Dirac fermions in SrMnBi_2 . This is further confirmed by the observation of a non-zero Berry phase ($=0.60(9)$) from Shubnikov-de Haas (SdH) oscillations that is expected to be 0.5 for Dirac fermions for a graphene monolayer[105]. As the Bi square net layer hosts Dirac fermions, the SOC gap size could be engineered by replacing Bi with other pnictogens with lower atomic numbers[71, 110]. Feng *et al.*[64] observed differences in Dirac cone structures of CaMnBi_2 and SrMnBi_2 originating from spin-orbit coupling and the arrangement of the Sr/Ca ions above and below the Bi square net layer which resulted in a larger gap size in SrMnBi_2 than in CaMnBi_2 .

It was thought earlier that the antiferromagnetic ordering of the Mn-atoms for the cases of $(\text{Sr}/\text{Ca}/\text{Eu})\text{MnBi}_2$ is crucial for the anisotropic behavior, but this has been ruled out after the observation of a Dirac cone like structure close to E_F along the $\Gamma - M$ direction in LaAgBi_2 [67–69]. However, magnetism seems to be essential for Dirac materials as the long-range magnetic order couples the Dirac fermions which influences the transport behavior[63] as observed from the differences in the magneto-transport behavior of SrMnBi_2 and CaMnBi_2 . Both materials possess Néel type in-plane AFM order, however, the neighboring MnBi_4 layers are coupled ferromagnetically in CaMnBi_2 and antiferromagnetically in SrMnBi_2 which results in a T_N anomaly in SrMnBi_2 , but not for SrMnBi_2 as shown in Fig. 14. The opposite interlayer couplings were claimed to originate from the competition between the AFM super-exchange and FM double-exchange interactions[63].

For the case of SrMnBi_2 and CaMnBi_2 , Mn-

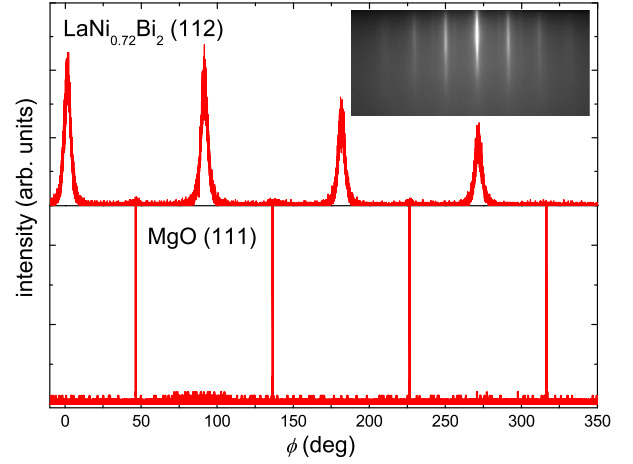


FIG. 17: In-plane X-ray (ϕ) scan of LaNi_xBi_2 grown on MgO substrate and (inset) RHEED image taken along the (110) direction of MgO after deposition[57]. Reprinted with permission from Buckow *et al.*[57]. Copyright 2013 by Institute of Physics.

atoms order antiferromagnetically[29] between 270 K and 290 K[31, 68] along the c -axis, which is different from the case of iso-structural EuMnBi_2 where Mn atoms order at 315 K and Eu-moments at $T_N = 22$ K[70]. A significant anisotropy enhancement was observed due to the interaction between Eu and Mn-moments that leads to a large increase in magnetoresistance $\sim 650\%$ at 5 K (12 T) which stays unsaturated at the highest applied field of 13 T at 5 K[70]. Transverse magnetoresistance behavior for SrMnBi_2 , CaMnBi_2 , LaAgBi_2 , SrZnSb_2 [30, 65, 67, 68, 71] goes thorough a semi-classical low field ($\sim B^2$) dependence to a linear ($\sim B$) dependence in the high-field limit around a critical field (B^*) as illustrated in Fig. 15. The quadratic temperature dependence of B^* can be attributed to Landau level splitting of the linear energy dispersion at high field, with magnetoresistive mobility comparable to that of graphene[30]. Linear magnetic field dependence of the MR supports the existence of a linear dispersion which for CaMnBi_2 is 105% at 10 T for $H \parallel c$ [66] and 120% at 9 T ($H \perp c$) and 2 K[65], for $\text{SrZnSb}_2 \sim 300\%$ at 9 T and 2 K[71]. Large magneto-thermopower was measured in SrMnBi_2 with a maximum change of 1600% at 9 T and 10 K. The sign of thermopower is positive for SrMnBi_2 and negative for CaMnBi_2 suggesting that hole and electron-type carriers are responsible for them respectively, although the thermal conductivity stayed independent of magnetic field[60]. The anisotropy and magnetoresistive behavior suggest the possible universal existence of Dirac fermion states in layered compounds with 2D double sized Bi square net layers[68].

VIII. Thin Films

High-quality thin films of pnictide compounds will be important for applications, however, they can also do as an useful alternative to those materials where single crys-

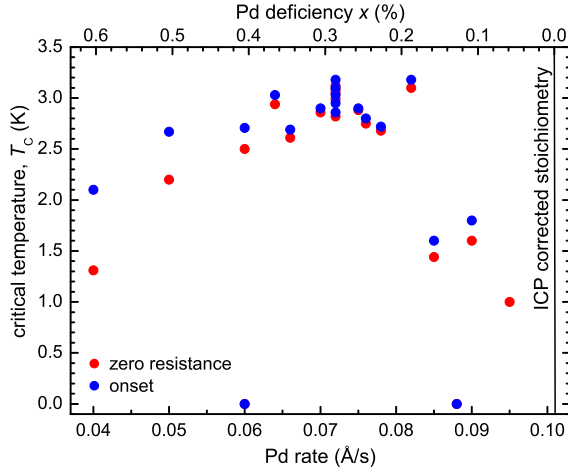


FIG. 18: Phase diagram of LaPd_xSb_2 showing the variation of T_c as function of the Pd content[55]. Reprinted with permission from Retzlaff *et al.*[55]. Copyright 2015 by American Physics Society.

tals are still unavailable. Single crystalline phases of pnictide superconductors were grown using MBE and pulsed laser deposition (PLD) showing that thin film techniques are useful for stabilising pnictide compounds (including metastable materials) by using growth kinetics and substrate induced epitaxial strain which is difficult to realize in bulk form. Superconducting films of 122 and 1111-phases of pnictides were grown successfully using PLD [111, 112] and, in some cases, higher crystallinity and superior superconducting properties were observed in thin films compared to their bulk counterparts [113, 114]. Recent observation of high- T_c (~ 65 K) in the 11-structure compound FeSe [26, 115–118] has fuelled interest in superconducting thin film systems. In situ measurements on a monolayer of FeSe grown on SrTiO_3 has revealed a $T_c > 100$ K [27] which is the highest (almost 10 times higher than bulk $T_c \sim 10$ K [12]) in any pnictide system observed so far. The superconductivity in FeSe films has been claimed to originate from interface mode coupling, thus, is most likely not a bulk effect.

A. Growth by Molecular Beam Epitaxy Technique

The first single-phase superconducting thin film of the 112-phase has been LaNi_xBi_2 grown by MBE[34]. MBE allows to grow a range of materials of various melting points using a combination of electron guns and (high-temperature) effusion cells. This is advantageous in terms of material flexibility, compositional and structural stabilisation as it allows precise doping control. The growth process was carried out in UHV atmosphere (typically at a base pressure $\sim 10^{-9}$ mbar) and typical substrate temperatures between 300 and 600°C. $\text{MgO}(100)$ substrates were found to be suitable for epitaxial growth of most of the systems studied[34, 55, 57, 58]. The substrates were pre-annealed at 1000°C in atmosphere to improve their surface quality. The growth process was monitored in situ using reflection high energy electron

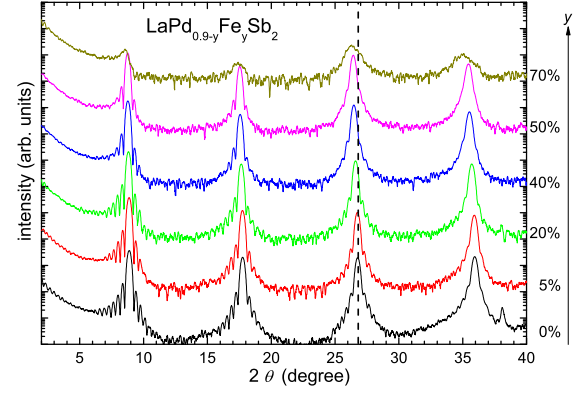


FIG. 19: Out-of-plane ($2\theta - \omega$) XRD scans of $\text{LaPd}_{0.9-y}\text{Fe}_y\text{Sb}_2$ for various Fe-doping level $0 \leq y \leq 0.7$ [55]. Reprinted with permission from Retzlaff *et al.*[55]. Copyright 2015 by American Physics Society.

diffraction (RHEED).

B. Thin Film Structure

A list of samples investigated in thin film form along with their growth parameters is shown in Tab. I. For all these materials, the out-of-plane X-ray diffraction (XRD) pattern (see Fig. 16(a)) consisted of a series of $(00l)$ peaks which suggests a ZrCuSiAs -type of crystal structure with the symmetry group $P4/nmm$. The 112-phase thin films were found to be highly c -axis oriented and phase pure resulting in some cases in a higher crystalline quality as compared to the bulk synthesised counterpart of the same material. The high crystalline nature of the films was confirmed by the observation of Laue oscillations (see Fig. 16(c)) with very narrow FWHM typically between 0.03 - 0.07° (see Fig. 16(b)). The presence of streaky lines in the RHEED pattern in Fig. 17 (inset) indicated the epitaxial nature of the films and smooth nature of the surface. From the X-ray ϕ -scan in Fig. 17, the four-fold symmetry of the tetragonal structure of the films were observed. In addition to the primary 4-peaks with 90° separation, another set of 4-peaks with reduced intensities were placed symmetrically between the primary peaks suggesting the presence of two sets of growth domains rotated by 45° to each other. It was concluded that the peaks with higher intensity correspond to the majority domains which overgrew the minority domains (corresponding to low intensity peaks) which are only present at the substrate/sample interface.

C. Superconducting and Magnetic Properties of Thin Films

The T_c was obtained from four probe resistivity measurements where a sharp superconducting transition was observed. At room temperature, all the films had a resistivity in the range of $100 \mu\Omega\text{cm}$. Between 5 K and 30 K, the resistivity shows metallic behavior that can be fitted using a quadratic temperature dependence $\rho(T) =$

Material	Substrate temperature (°C)	Growth rate (Å/s)	Lattice constant in-plane (Å)	Lattice constant out-of-plane (Å)	T_c (K)
LaNi _x Sb ₂ [57]	390-450	~ 0.5	4.57±0.1	9.76±0.01	4.05
CeNi _x Bi ₂ [34]	410-440	~ 0.5	4.565±0.002	9.64±0.01	4.05
LaNi _x Bi ₂ [58]	400-450	0.25-1.0	-	9.786	3.1
LaPd _x Sb ₂ [55]	440-520	-	4.52(2)	9.88(5)	3.27
LaPd _x Bi ₂ [55]	405-445	-	4.55	9.70(9)	3.03

TABLE I: List of 112-type pnictide superconducting thin films and their growth parameters.

$\rho_0 + AT^2$, and from 30 K to 300 K, the $\rho(T)$ vs. T dependence is mostly linear. The small residual resistivity ratio [55] (~ 1.58) indicated a good quality and crystallinity of the samples. Magnetic measurements revealed the presence of Meissner shielding at $T < T_c$ with a significant volume of the superconducting phase. For LaPd_xSb₂, the lower and upper critical fields were about 10 G and 1.1 T, respectively (with the field applied in out-of-plane direction).

The superconducting phase has been found to depend on the stoichiometric variation of its constituting elements. For LaPd_xSb₂ within a $\pm 5\%$ variation of the optimal Sb concentration, T_c stayed almost unaffected, while for larger variations superconductivity vanished associated with a sharp decline in crystallinity. However, for variation in Pd concentration T_c showed a broad dome-shaped behaviour around the mean-value where highest T_c is observed as shown in Fig. 18. The influence of Fe substitution on the structural behaviour of LaPd_xSb₂ has been illustrated in Fig. 19. Replacement of Pd by Fe in LaPd_{0.9-y}Fe_ySb₂ led to a sharp decline in crystallinity for $y > 0.5$ indicated by the disappearance of Laue oscillations as shown in Fig. 19, by a shift of the (003) peak position, and also by an increase in the c -axis lattice constant. Superconductivity disappeared instantly even on a small level ($\sim 5\%$) of Fe substitution in LaPd_xSb₂, which suggests a conventional s -wave nature of the superconducting state as a small amount of ferromagnetic impurities lead to a strong reduction of the BCS density of states. So far, thin films of high- T_c 112-pnictides are elusive. Such films could be a new playground for investigating the symmetry of the order parameter and achieving critical temperatures above 77 K.

IX. Conclusion and outlook

In this review, we have summarised the investigation of superconductivity and Dirac fermions in 112-type pnictides. The existence of naturally occurring anisotropic Dirac Cones in the intermetallic 112-structure makes them interesting for possible application in nanoelectronics as an alternative to graphene while the large magnetoresistance could be of interest for spintronics. The discovery of high- T_c superconductivity in Ca_{1-x}La_xFeAs₂ [16] has generated significant research interest in this newly discovered Fe-based super-

conducting system. Structurally the 112-phase is quasi-2D similar to the 1111-phase, but the presence of a metallic spacer layer and multiple-vacancies of the Pn -atoms in the neighboring layers are unique properties of this system. Although the parent compound CaFeAs₂ has not been synthesised yet, superconductivity can be introduced by RE -doping and the T_c has been predicted to go beyond 50 K for smaller levels of RE -content in Ca_{1-x}RE_xFeAs₂ [18]. Evidence of a structural and a magnetic phase transition were found both in the non-superconducting and superconducting phases [51, 54, 77]. ARPES measurements revealed the presence of three hole like Fermi pockets at the zone centre and two electron like pockets at the zone corner with $3d$ character similar to the other pnictide systems with moderate nesting between them [16, 53, 78, 79]. In the low- T_c 112-systems, T_N lies below 10 K and the presence of Ni-vacancies in the Ni_xBi layer seems to be crucial to stabilize the crystal structure and bulk superconductivity [33]. For Ca_{1-x}La_xFeAs₂, T_N can be enhanced up to 70 K [51] for a high level of RE -doping.

In general, Sb doping helps increasing the in-plane lattice constants. A larger sized pnictogen results in a T_c enhancement with increased superconducting volume fraction for various RE -doped Ca_{1-x}RE_xFeAs₂ with the so far highest T_c of 47 K. Preliminary measurements suggested a conventional s -wave type of pairing symmetry in the 112-phase, although a small amount of TM doping seems to improve the superconducting properties in some cases. The moderate level of anisotropy in the 112-phase Ca_{1-x}La_xFeAs₂ lies in between the 1111 and 122-type pnictide systems, while the upper critical field is significantly higher than for other pnictide phases with comparable critical current density. This makes it interesting from an application perspective as J_c can reach 10^6 A/cm² over a large magnetic field range which sounds promising for the fabrication of superconducting tapes and Josephson junctions [47]. Also, it will be interesting to see if the substrate generated strain and interface effects can improve the T_c in a thin film structure similar to the FeSe thin films. Generally, due to the lower level of RE -elements the 112-phase will allow significant cost reduction in producing superconducting tapes compared to the 122/1111-pnictide phases. For this purpose, the long-time stability of the 112-compounds will be essential.

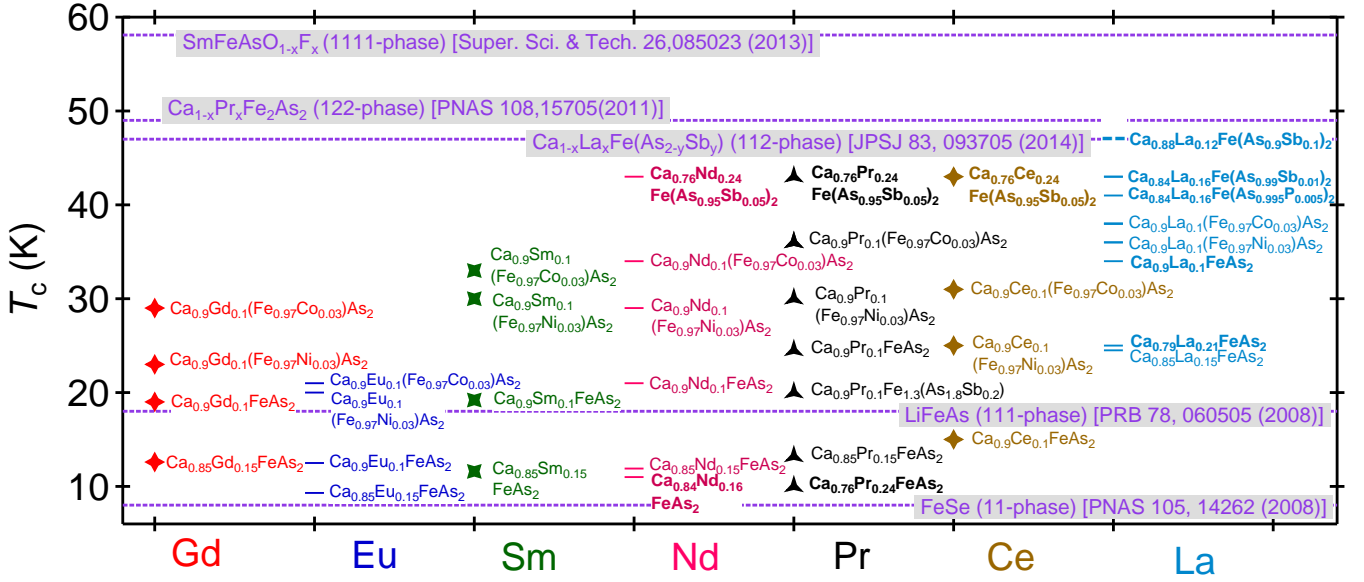


FIG. 20: A phase diagram based on the T_c values of various $(\text{Ca}, \text{RE})\text{FeAs}_2$ phases for various RE-elements, arranged in the order of increasing ionic radii under various doping conditions. Symbols indicate T_c values reported so far for various single crystalline (labels in bold fonts) and polycrystalline phases [16–18, 40, 42, 48, 49, 72]; horizontal dotted lines indicate the maximum T_c values reported for various types of pnictide phases.

Compared to the other pnictide phases, the research work on the 112-system is still at a relatively younger stage and further investigation is needed to understand the potential of this pnictide phase. A list of the T_c 's of various 112- $(\text{Ca}, \text{RE})\text{FeAs}_2$ compounds studied so far has been illustrated in Fig. 20. General trend can be found that larger the size of the RE-ion, higher is the T_c . It is agreed that further reduction of the RE-content is essential for the further enhancement of T_c in the $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ system which : (a) for the bulk system needs further optimisation of the solid state synthesis techniques and (b) could be possible through various thin film growth processes, but yet to be explored for the $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ system. Scattering techniques like μSR [119, 120] and Small Angle Neutron Scattering (SANS) could be useful to explore various parts of the phase diagram : (a) to understand the microscopic presence of magnetism and superconductivity and (b) nature of the vortex lattice symmetry and the vortex phase diagram. It can be expected that the availability of good quality and

larger sized single crystals and thin films will allow diverse investigation in this system. Understanding the exact role of Sb on the enhancement of T_c will help achieving higher T_c in future. In an ideal case, Sb could replace As completely in superconducting 112-compounds with T_c above 77 K paving the way for a sustainable use of pnictide superconductors in applications.

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